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Preparation of porous chitosan gel beads for copper(II) ion adsorption

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Abstract

In this paper, chitosan porous beads were prepared by using a phase inversion technique, and then used for the adsorption and removal of copper(II) ions. The porosity, diameter and other characteristics were characterized. With the increase of chitosan and NaOH concentration used to prepare the beads, the amount of adsorbed Cu^{2+} per gram of the beads decreased. A maximum adsorption amount was observed at a pH value of 6.0 for the cross-linked porous chitosan beads. The amount of the adsorbed Cu^{2+} increased with the Cu^{2+} concentration used in the adsorption experiments. By the relationship of the ratio of the equilibrium Cu^{2+} concentration in the solution (C_e) to the adsorbed equilibrium amount (P_e) (C_e/P_e) and C_e, we concluded that the adsorption of Cu^{2+} to the porous chitosan beads was Langmuir adsorption. The Cu^{2+}-loaded porous chitosan beads were stable in water, which is useful for further study on selectively adsorption of IgG. The results suggested that the porous chitosan beads were useful adsorbents for copper ions removal in water treatment, and the Cu^{2+}-loaded beads may be good sorbents for IgG removal in blood purification.

Keywords: Phase inversion; Chitosan porous beads; Copper ions; Adsorption

1. Introduction

Waste streams containing low-to-medium level of heavy metals are often encountered in industries. Most of heavy metals must be removed from the contaminated water in order to meet increasingly stringent environmental quality standards due to their high toxicity and un-biodegradability. Many methods have been used to treat such effluents but most of them are either expensive or incapable of removing trace level of heavy metal ions. Adsorption is one of the few promising alternatives for this purpose, especially using low-cost bio-sorbents such as agricultural wastes, clay materials, biomass, and seafood processing wastes [1,2].

Chitosan is just one of the most representative biopolymers, receiving considerable interest for heavy metals removal due to its excellent metal-binding capacities and low cost in recent years. Chitosan, poly(*b*-1-4)-2-amino-2-deoxy-D-glucopyranose, is produced by partially alkaline *N*-deacetylation of chitin, which can be widely found in the exoskeleton of shellfish and crustaceans as the second most abundant natural biopolymers next to cellulose [1]. It is known as an outstanding sorbent of extremely high affinity for transition and post transition metal ions selectively because the amino ($-NH_2$) and/or hydroxy ($-OH$) groups on chitosan chains serve as coordination sites [2,3].

It has been reported that heavy metal ions could be effectively removed by chitosan beads or flakes [4–6]. A comparative study on the adsorption capacity of chitosan for various metal ions such Cu^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, and Hg^{2+} was conducted. It was found that chitosan exhibits the highest binding capacity for Hg^{2+} and Cu^{2+}, and 17.0 mg Cu^{2+} was adsorbed onto 1 g chitosan [4]. In another study, the adsorption of copper on chitosan was also studied and it was found that 1 g chitosan could adsorb 4.7 mg of Cu^{2+} at pH of 6.2 [5]. The adsorption capacity of copper by the chitosan shows significant difference among the reports. The difference in chitosan adsorption capacity between the studies could be due to the difference of the preparation process and the particle size of the particles used in the study.

Chitosan gel beads can be easily prepared by a common phase inversion method [7]. In general, chitosan is dissolved in an acidic solution, and then the solution is dropped into a

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Nomenclature

a_L	the Langmuir constant incorporating the enthalpy of sorption (L/mg)
C	bulk Cu(II) concentration at indicated time (mg/L)
C_e	equilibrium Cu(II) concentration (mg/L)
C_0	initial Cu(II) concentration (mg/L)
P	amounts of Cu(II) adsorbed (mg/g)
P_e	the equilibrium amount of Cu(II) adsorbed on chitosan beads (mg/g)
P_{max}	the maximum saturation capacity or "Langmuir" monolayer sorption capacity (mg/g)
Q	amounts of Cu^{2+} desorbed (mg/g)
R	final diameter of chitosan gel bead (mm)
R_0	original diameter of chitosan–HAc solution (mm)
V	volume of Cu(II) solution (L)
W_D	weight of dried chitosan gel bead (g)
W_W	weight of wet chitosan gel bead before drying (g)
W_0	weight of original chitosan–HAc solution (g)
X_{HAc}	weight percentage of acetic acid in chitosan–HAc solution
X_R	diameter decreasing during the preparation
X_W	The change of water weight in the beads during the preparation

Greek letters

ρ_{Ch}	density of chitosan, $\rho_{Ch} = 0.47\ g/cm^3$
$\rho_{Ch\text{–}HAc}$	density of chitosan–HAc solution (g/cm^3)
ρ_S	density of final Cu(II) solution, $\rho_S = 1.0\ g/cm^3$
ρ_W	density of water, $\rho_W = 1.0\ g/cm^3$

non-solvent of chitosan. After the exchange of the solvent and the non-solvent, porous chitosan beads are prepared. Though the general method was used for the preparation of chitosan beads, the preparation conditions like reagent concentration were chosen randomly by different researchers [8–11].

The porosity and strength of the beads correspond to the concentration of the chitosan–acid solution, the degree of *N*-deacetylation of chitosan, and the type and concentration of the precipitate agents used [12]. Up to now, despite a large number of papers dedicated to the sorption of metal ions by chitosan, most of them focus on the evaluation of sorption performances altered by chemical modification on the amino groups or sorption mechanism, but little aim at gaining a better understanding of the coacervation process from solution to gel beads.

In the present study, we systematically investigate how the preparation conditions influence the shape and the structure of the porous beads, and their effects on the sorption properties (uptake kinetics and sorption capacity). The effects of chitosan and acetic acid (HAc) concentration in the chitosan–HAc solution and NaOH concentration (precipitation medium) on the physical properties and performance of Cu(II) uptake were examined. The pH effects and the stability of the adsorbed Cu(II) were also examined, which are for further study of selectively adsorption of IgG by the Cu(II)–chitosan porous beads.

2. Materials and methods

2.1. Materials

Chitosan powder was purchased from Boao Biological Tech. Co. Ltd., Shanghai, with a deacetylation degree of about 90% and viscosity below 100 cps. Acetic acid (HAc), sodium hydroxide (NaOH), cupric sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), glutaraldehyde were supplied by Kelong Chemical Reagents Factory, Chengdu. All the regents are analytical-reagent grade, and were used without further purification.

2.2. Preparation of porous chitosan gel beads

Chitosan–acetic acid solution was prepared by dissolving required amount of chitosan powder into corresponding aqueous acetic acid solution. Then, the solution was dropped into a precipitation bath containing 500 ml of 0.5, 1 or 5 mol/L aqueous sodium hydroxide solution, by using a 0.4 mm diameter syringe needle, and stirred using a magnetic stirrer. The injection speed was controlled at about 60 drops/min. The air gap from the needle to the surface of the NaOH solution was 10 cm. After half an hour, the transparent nascent beads became opaque, and solidified; then the wet chitosan beads were collected and extensively rinsed with distilled water to remove any NaOH, and stored in distilled water until use. Several kinds of chitosan beads are prepared using different chitosan concentrations as listed in Table 1.

For the study of pH effect on the adsorption, the chitosan porous beads were cross-linked by glutaraldehyde using a similar procedure to that described by Wan Ngah et al. [8].

2.3. Calculation of the diameter and porosity of the beads

The diameter (R) and the porosity of the beads were calculated from the density of the chitosan and the weight change before and after drying [7], using the following formulas:

$$R = \left[6\frac{W_D/\rho_{Ch} + (W_W - W_D)/\rho_W}{\pi}\right]^{1/3}$$

$$\text{Porosity} = \frac{(W_W - W_D)/\rho_W}{W_D/\rho_{Ch} + (W_W - W_D)/\rho_W}$$

where W_W (g) is the weight of the wet chitosan gel bead before drying; W_D (g) the weight of the dried chitosan gel bead; ρ_W ($\rho_W = 1.0\ g/cm^3$) the density of water; and ρ_{Ch} ($\rho_{Ch} = 0.47\ g/cm^3$) is the density of the chitosan.

2.4. Scanning electron microscopy (SEM)

For SEM observation, the porous beads were freeze–dried at −20 °C for 2 months. Then cut with a single edged razor blade,